

AD-A102 426

NEW YORK UNIV N Y DEPT OF CHEMISTRY
PHOTOELECTRON EMISSION SPECTROSCOPY OF AQUEOUS SOLUTIONS.(U)
JUN 81 P DELAHAY

F/G 7/4

N00014-75-C-0397

NL

UNCLASSIFIED TR-16

Line 1
AP-A
10-242

END
DATE
8-81
DTIC

DTIC FILE COPY

AD A102426

LEVEL

12

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0397

Task No. NR 051-258

9 TECHNICAL REPORT NO. 16 (New Series)

14 TR-16

6 Photoelectron Emission Spectroscopy of
Aqueous Solutions,

by

10 Paul Delahay

Prepared for Publication

in

Accounts of Chemical Research

DTIC
ELECTED
AUG 4 1981

New York University
Department of Chemistry
New York, NY

11 Jun 1981

12 32

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

406 517

81 8 04 014

mit

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 16 (New Series)	2. GOVT ACCESSION NO. <u>AD-A102 426</u>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) PHOTOELECTRON EMISSION SPECTROSCOPY OF AQUEOUS SOLUTIONS	5. TYPE OF REPORT & PERIOD COVERED Technical Report	
7. AUTHOR(s) Paul Delahay	6. PERFORMING ORG. REPORT NUMBER N00014-75-C-0397	
9. PERFORMING ORGANIZATION NAME AND ADDRESS New York University New York, NY 10003	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-258	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217	12. REPORT DATE June 1981	
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	13. NUMBER OF PAGES 32	
	15. SECURITY CLASS. (of this report)	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17 DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Accession Form
NTIS CBA&I
PTIC TAB
Unannounced
Justification

18 SUBRI ELEMENTARY NOTES

Submitted for publication in Accounts of Chemical Research

By

Distribution/

Availability Codes
Avail and/or
1st Special

Answers

Aqueous solutions

EMISSION spectrum Photoelectron spectroscopy

Photoelectron spectroscopy Reorganization free energy

The cashed-up economy

Threes Mates

(Indicate all necessary and identify by block number)

Review of current work on photoelectron emission spectroscopy of aqueous solutions. Theoretical background covers: free energy of emission, threshold energy for emission, reorganization free energy. Applications include: water and hydroxide ion, anions, cations, weak acids and bases and their ions.

Photoelectron Emission Spectroscopy of Aqueous Solutions

Paul Delahay

Department of Chemistry, New York University, 4 Washington Place, Room 514,
New York, NY 10003

Received

Irradiation of the surface of a liquid or a solution with photons of sufficient energy causes the emission of electrons into the gas phase above the liquid. Electrons can be collected by means of an electrode located in the vapor phase above the liquid, and an emission spectrum can be determined by varying the photon energy. Irradiation in the vacuum ultraviolet range at wavelengths as short as 115 nm is necessary with most aqueous solutions. New and significant results were recently obtained by this method: experimental separation of fast (electronic) and slow (nuclear) relaxation in ionic solvation, production and characterization of unusually high oxidation states of metals generated by photoionization in aqueous solution, information about the protonation of radicals produced by photoionization of weak acids and bases and their ions in aqueous solution. These and other results are discussed in the present Account.

A few comments may be helpful to show how experiments are performed. Details are given in reference 1. The continuously renewed liquid film on the flange of a rotating quartz disk (Figure 1) is irradiated through a lithium fluoride window. The disk assembly is contained in an evacuated enclosure. The solution is cooled (ca. 2°C) to lower the vapor pressure and minimize attenuation of the photon flux by water vapor in the gap between the lithium fluoride window and the rotating disk. The photon flux is monitored by means of a sodium salicylate crystal C (vacuum ultraviolet to visible

conversion) and a photomultiplier detector located behind the glass window G. Both the photomultiplier current and the current collected by the electrode (gold grid mesh, 80% transparency) in the vapor phase are measured as a function of the photon energy E. The emission yield Y is computed and expressed as the number of collected electrons per incident photon at a given E. Results are displayed as an emission spectrum consisting of a plot of Y against E (Figure 2).

Free Energy of Emission

The energetics of photoelectron emission by a solution will be discussed first, and the fundamental equation for the interpretation of experimental results will be obtained. This will be done for a concrete example, namely an aqueous solution of chloride ions (e.g., potassium chloride), but the treatment is readily transposed to anions in general, electrically neutral species and cations.

Photoelectron emission is represented by the equation,



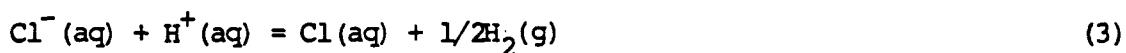
where the notations (aq) and (g) denote species in solution and the gas phase, respectively. Photoionization is a "vertical" process (Franck-Condon principle), and therefore the chlorine atom initially retains the solvation nuclear configuration of the chloride ion. Conversely, the chlorine atom produced by reaction 1 has the solvation electronic configuration of an electrically neutral substance. Thus, changes in nuclear configuration of solvent molecules are slow on the scale of time considered here whereas changes of electronic configuration are fast. The transient configuration of the solvent molecules is denoted by (aq_{*}) in eq 1. The solvation nuclear configuration about Cl(aq_{*}) relaxes according to



and a solvated chlorine atom is obtained by photoionization. This atom may undergo further reaction, but such subsequent process need not concern us at this stage. Relaxation from vibrationally excited states must also be considered in addition to relaxation of solvent orientation when diatomic or polyatomic molecules or ions are photoionized.

Process 1 bears some resemblance to photoelectron emission by a metal. The latter is characterized by the work function of the metal, that is, the work done in transferring an electron from the electrically uncharged metal to infinity in vacuum. The counterpart of the work function for process 1 is the free energy of emission ΔG_e . This quantity is positive and pertains to a vertical process. Conversely, process 2 involves a negative change of free energy designated as the free energy of reorganization. The quantity ΔG_r includes a contribution from vibrational relaxation for diatomic or polyatomic species.

The sum $\Delta G_e + \Delta G_r$, which is smaller than ΔG_e since $\Delta G_r < 0$, is the change of free energy for the adiabatic process (in the spectroscopic sense) represented by the sum of reactions 1 and 2. This adiabatic process can also be regarded as the sum of the following two reactions,



involving the changes of free energy ΔG and ΔG_H , respectively. The value of ΔG can readily be calculated from thermodynamic data in the particular case of reaction 3. This, however, is not possible in most cases because the relevant data are not available, e.g., for the oxidation of $\text{SO}_4^{2-}(\text{aq})$ to $\text{SO}_4^-(\text{aq})$ (with emission of a photoelectron).

The free energy ΔG for reaction 3 is expressed according to the usual convention of assigning zero free energies of formation to $1/2\text{H}_2(\text{g})$ and

$\text{H}^+(\text{aq})$ under standard conditions. Electrons are emitted into the gas phase in our case, and the free energy of formation of the electron $e^-(\text{g})$ must be expressed in a way consistent with eq 3. This is done by introducing reaction 4. The change of free energy for this reaction, $\Delta G_{\text{H}} = 4.50 \text{ eV}$, was calculated by Noyes,² and consequently the standard free energy of formation of $e^-(\text{g})$ is 4.50 eV. The preceding value of ΔG_{H} does not include the contribution from the surface potential at the solution-water vapor interface. The surface potential will be neglected here since it is small ($\pm 0.1 \text{ V}$ for water³) and nearly cancels out when differences of free energies of emission are considered.

The processes represented by reactions 1 plus 2 and reactions 3 plus 4 are equivalent, and the corresponding changes of free energy $\Delta G_e + \Delta G_r$ and $\Delta G + \Delta G_{\text{H}}$ must be equal. Hence,

$$\Delta G_e = \Delta G_{\text{H}} + \Delta G - \Delta G_r. \quad (5)$$

This general equation is of fundamental importance in photoelectron emission spectroscopy, as will be evident from the present Account. Equation 5 is implicitly contained in the work of Henglein and coworkers.^{4,5} Ballard⁶ reported an equation similar to eq 5. The ΔG_r term was not included but was briefly discussed, and the value $\Delta G_{\text{H}} = 4.39 \text{ eV}$ was obtained from consideration of two consecutive reactions equivalent to 4. Equation 5 was applied extensively in recent papers from this laboratory.⁷⁻⁹

Equation 5 clearly shows the relationship between photochemical and electrochemical oxidation.⁴⁻⁹ The change of free energy ΔG pertains to reaction 3 written as an oxidation, and consequently the reduction potential for the $\text{Cl}(\text{aq})/\text{Cl}^-(\text{aq})$ couple is $E = \Delta G/|e|$ (no minus sign!), where e is the electronic charge and E is expressed with reference to the normal hydrogen electrode. The term ΔG_{H} in eq 5 can be regarded as a change of "reference

electrode." The positive quantity $-\Delta G_r$ ($\Delta G_r < 0$) appears in eq 5 because $\Delta G_H + \Delta G$ pertains to an adiabatic process whereas photoelectron emission is a vertical process.

Threshold Energy for Emission

The central problem is to determine some characteristic energy from emission spectra and to find the relationship between this energy and ΔG_e of eq 5. This problem was solved only recently although the idea of studying photoelectron emission by solutions dates back (1888) to the early work on the photoelectric effect (historical background in reference 10). Three conditions had to be fulfilled: (i) A theory became available for the analysis of emission spectra. (ii) Transport of electrons in the gas phase was understood.¹¹ (iii) Instrumentation was developed¹ for the determination of emission spectra of aqueous solutions in the vacuum ultraviolet range. Only the first of these three problems will be discussed in some detail. Transport of electrons in the gas phase does not pose any serious problem, and instrumentation was briefly discussed after the introductory remarks.

The theory of photoelectron emission by liquids and solutions was developed in several stages. A three-step model for emission, which was inspired from solid-state physics, was proposed initially by the author.¹² Emission was considered as a sequence of the following three consecutive steps: (i) generation of mobile (quasifree) electrons by photoionization of a species (solute, solvent) in the liquid phase; (ii) random walk of mobile electrons with loss of kinetic energy to the liquid medium; (iii) crossing of the liquid-vapor interfacial barrier by the mobile electrons reaching it. A phenomenological equation for the emission current derived from this model provided a qualitative understanding of emission spectra.¹² An essential

feature of the experimental method also follows from this model. Thus, electrons are emitted into the gas phase from a layer of solution having a thickness of the order of the thermalization length of low-energy (a few electronvolts at most) electrons in aqueous solution. This length is ca 2 to 4 nm, and consequently there is hardly any attenuation of the photon flux as a result of absorption by water in the layer from which emitted electrons originate. Conditions of a thin-layer technique are achieved.

The three-step model was developed further by treating electrons generated by photoionization either as classical particles or according to quantum mechanics. The classical approach developed by Neme¹³ proved valuable in the analysis of energy distribution curves ¹⁴ (not reviewed here) but was not useful for the analysis of emission spectra. The quantum theory of Brodsky and Tsarevsky¹⁵ was very successful in this respect. The transport of electrons in this theory is treated as the propagation of a wave, and the interaction with the medium is accounted for by an exponential attenuation factor. Both transmission through the interfacial barrier and reflection by this barrier are considered. The theory was criticized, not without reason, for its treatment of image forces¹⁶ and its neglect of fluctuations.¹⁷ Yet, the extrapolation method based on the Brodsky-Tsarevsky theory is amazingly successful in the analysis of emission spectra of aqueous solutions. Thus, a plot of Y^n against the photon energy E (Figure 2), where $n = 0.4$ or 0.5 , is linear, and extrapolation to $Y^n = 0$ yields the threshold energy E_t (Table I). Departure from linearity very near E_t arises from simplifications inherent to the theory. The linear plots with $n = 0.4$ and $n = 0.5$ correspond to two limiting cases of a more general equation given in reference 15. The choice of n depends on the range of kinetic energy of electrons, but the theoretical criteria are too stringent. In practice, data

are processed by computer, and the best value of the exponent, $n = 0.4$ or 0.5 , is determined by means of statistical analysis (F-test,¹⁸ Figure 2). As a rule of thumb, one has $n = 0.4$ for $E_t < 8$ eV and $n = 0.5$ for $E_t > 8$ eV for aqueous solutions. Linear extrapolation plots have been obtained in this laboratory with extremely good statistics for numerous ions and molecules in aqueous solution, and the linearity of the extrapolation plots is well established even if some aspects of the underlying theory can be argued.

Threshold energies were correlated to free energies of emission by recourse to experiment.^{7,9} The Cl^- , Br^- and I^- ions in aqueous solution were selected for this purpose because both ΔG (2.51, 1.98, 1.32 eV, respectively) and ΔG_r (-1.74, -1.57, -1.36 eV) of eq 5 can be calculated quite accurately from independent data. Thus, one computes from eq 5, $\Delta G_e(\text{Cl}^-) = 8.75$ eV, $\Delta G_e(\text{Br}^-) = 8.05$ eV, $\Delta G_e(\text{I}^-) = 7.18$ eV versus $E_t(\text{Cl}^-) = 8.81$ eV, $E_t(\text{Br}^-) = 8.05$ eV, $E_t(\text{I}^-) = 7.19$ eV. The relationship, $\Delta G_e \approx E_t$, therefore holds for these ions, even if one allows for the uncertainty from the neglect of the surface potential (cf. discussion of eq 5). This conclusion, in the general case, can be justified qualitatively in terms of the Gurney-Gerischer formalism developed by Henglein^{4,5} for electron transfer in solution, but this analysis is beyond the scope of this Account. In conclusion, there is no reason to doubt that the equation $\Delta G_e \approx E_t$ holds in general (within a few tenths of electronvolt or even better).

Reorganization Free Energy

The reorganization free energy ΔG_r will be interpreted by following the opposite approach to the one at the end of the preceding section. Thus, ΔG_e will be equated to E_t , and ΔG_r will be calculated from eq 5 for systems for which ΔG is known. This will be done⁸ for photoionization of the five

cations M^{2+} of Figure 3. The threshold energy in that case varies almost linearly with ΔG , and the calculated values of ΔG_r are nearly the same (-2.05 to -2.25 eV). In general, however, ΔG_r varies significantly from one species to another even for a series of chemically similar substances (e.g., for the halides discussed in the preceding section). Plots of E_t against ΔG for such a series are not linear in general, and even if they appear linear they do not have a unit slope. The general rule holds nevertheless that the reduced form of a strongly reducing redox couple ($\Delta G < 0$) has a low (ca 6 to 7 eV) threshold energy. Conversely, a high value of E_t (ca 8 eV) is obtained for the reduced form of a strongly oxidizing redox couple ($\Delta G > 1$ to 2 eV). These limits are, of course, approximate.

Reorganization free energies cover the range $-2.3 < \Delta G_r < -0.3$ eV for the substances studied thus far in aqueous solution. The limit of ca -2.3 eV corresponds, for instance, to ions such as M^{2+} in Figure 3. The lowest absolute value of 0.3 eV pertains to bulky ions with multiple charge such as $W(CN)_8^{4-}$. Analysis of the emission spectrum of this ion¹⁹ yields $E_t = 5.39$ eV and $\Delta G_r = -0.32$ eV ($\Delta G = 0.57$ eV). The cyanometalate complexes generally have rather small reorganization free energies (ca. -0.3 to -0.7 eV) and low threshold energies (< 6 eV), and irradiation in the ultraviolet range is sufficient to cause photoelectron emission. Thus, the ion $Fe(CN)_4^{4-}$, for instance, was found long ago¹⁰ (1923) to display emission: $E_t = 5.53$ eV, $\Delta G = 0.36$ eV, $\Delta G_r = -0.67$ eV (from the analysis of the emission spectrum in reference 19).

The reorganization free energy will be interpreted and correlated with ionic solvation.⁸ The latter is characterized by the real free energy of solvation ΔG_s defined as³ "the free energy change in the process where an ion in field-free space is inserted into a large quantity of solution which

carries no net electrical charge." Values of ΔG_s can be calculated from thermodynamic data^{2,3} with additional considerations outside the realm of thermodynamics. One has,² for instance, $\Delta G_s(\text{Fe}^{2+}) = -19.63 \text{ eV}$ and $\Delta G_s(\text{Fe}^{3+}) = -44.87 \text{ eV}$ for aqueous solutions. Solvation involves changes in both the electronic and nuclear configurations of solvent molecules. Conversely, the reorganization process in the photoelectron emission by Fe^{2+} ions, for instance, involves only the relaxation of the nuclear configuration of solvent molecules following the change of ionic charge from 2+ to 3+. The contribution from nuclear relaxation, $\Delta G_r = -2.11 \text{ eV}$ for Fe^{2+} (Figure 3), is only a small fraction of the difference of real free energies of solvation, $\Delta G_s(\text{Fe}^{3+}) - \Delta G_s(\text{Fe}^{2+}) = -44.87 + 19.63 = -25.24 \text{ eV}$, namely $(-2.11)/(-25.24) = 0.084$. The Franck-Condon principle was applied in reaching this conclusion, but no model of the solvation process was introduced. Determination of ΔG_r by means of photoelectron emission spectroscopy thus provides an experimental method of separating fast (electronic) and slow (nuclear) relaxation in ionic solvation. This is a significant result.

The preceding results will be reformulated by treating the solvent as a continuous medium undergoing electronic and orientation polarization as a result of ionic solvation. The real free energy of solvation is then given by the Born equation. The approach is quite crude but straightforward. Better models and methods of calculation are available²⁰ but are not needed for our purpose. Consider photoelectron emission by species A^{z+} ($z \geq 0$) in solution, and assume that the radii of the A^{z+} and $\text{A}^{(z+1)+}$ ions are equal to simplify matters. One deduces from the Born equation,

$$\begin{aligned} R &= \Delta G_r / (\Delta G_s^{z+1} - \Delta G_s^z) \\ &= (\epsilon_0^{-1} - \epsilon_s^{-1}) / (1 - \epsilon_s^{-1}), \end{aligned} \quad (6)$$

where ϵ_0 and ϵ_s are, respectively, the optical and static dielectric

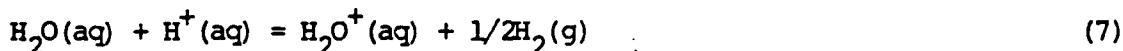
constants of the solvent. One has $\epsilon_0 = 1.777$ and $\epsilon_s = 78.36$ for water at 25°C, and $R = 0.56$ in that case. This is roughly the value of R for emission by singly charged anions⁹: $R = 0.50, 0.49, 0.48$, respectively, for Cl^- , Br^- , I^- ; $R = 0.44$ to 0.51 for OH^- depending on the estimate of $\Delta G_s(\text{OH}^-)$. The value $R \approx 0.50$ also holds for emission by liquid water,⁹ that is, for emission by an electrically neutral species. The change of free energy for orientation polarization ΔG_r in these cases corresponds approximately to one-half of the difference between the real free energies of solvation in eq 6. In contrast with the preceding cases ($z = -1$ or 0), the ratio R is much smaller than 0.56 for cations ($z = 1, 2, \dots$) and anions with multiple ionic charge ($z = -2, -3, \dots$). The change of free energy for orientation polarization ΔG_r in those cases is only approximately one-tenth of the difference between the real free energies of eq 6. This is indeed a drastic departure from the Born model.

The abnormally low values of the ratio R were interpreted⁸ as the consequence of strong dielectric saturation. The static dielectric constant ϵ_s decreases as a result of saturation and approaches the optical constant ϵ_0 . In the limit, one has $R \rightarrow 0$ for $\epsilon_s \rightarrow \epsilon_0$ for the Born model. For instance, one calculates (eq 6) $\epsilon_s = 1.91$ from the value $R = 0.084$ for emission by Fe^{2+} on the simplifying assumption that the radii of Fe^{2+} and Fe^{3+} are the same. The Born model undoubtedly breaks down, but the foregoing conclusion about a drastic effect of dielectric saturation seems inescapable. The same conclusion was reached by Noyes² in his work on the real free energies of solvation of inorganic cations and anions. His conclusion based on a formal application of the Born equation is fully confirmed in our work^{8,21} by evidence free of model considerations (cf. the case of Fe^{2+} above).

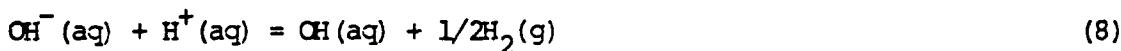
Dielectric saturation causes the threshold energies of cations and multiply charged anions to be much lower than the values to be expected ($E_t > 10$ eV in general) without saturation. Moreover, emission with formation of unusual oxidation states such as Cu(III) and Fe(IV) in aqueous solution (Table I) would hardly be possible without strong dielectric saturation.

Water and Hydroxide Ion

The threshold energies of liquid water⁹ and hydroxide ion^{7,9} in aqueous solution are 10.06 and 8.45 eV, respectively. The difference between these threshold energies will be interpreted⁹ on the basis of the free energy diagram of Figure 4. The free energies of formation of liquid water and OH⁻(aq) ions differ by $0.0592 \log 10^{-14} = 0.83$ eV on account of the dissociation of water. The free energy change ΔG for the reaction



was estimated at 3.3 ± 0.3 eV on the basis of the emission results. The value of $\Delta G = 1.97$ eV for the reaction



is known from thermodynamic data. One concludes from the preceding data that the change of free energy for the reaction



is -0.5 ± 0.3 eV. Thus, the ion H₂O⁺(aq) is thermodynamically unstable, and the hydroxyl radical OH(aq) does not protonate to any extent. These conclusions are consistent with experimental kinetic data.⁹

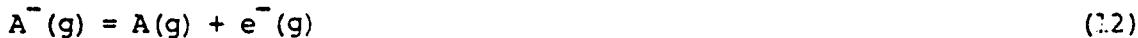
The difference in threshold energy for H₂O and OH⁻(aq) follows directly from Figure 4 and eq 5 (with $\Delta G_e \approx E_t$), namely

$$\begin{aligned} E_t(\text{H}_2\text{O}) - E_t(\text{OH}^-) &= [\Delta G(\text{OH}^-) - \Delta G(\text{H}_2\text{O})] \\ &\quad + [\Delta G(\text{H}_2\text{O}^+) - \Delta G(\text{OH})] + [\Delta G_r(\text{OH}) - \Delta G_r(\text{H}_2\text{O}^+)] \\ &= 0.83 + 0.50 + 0.28 \\ &= 1.61 \text{ eV} \end{aligned} \quad (10)$$

The notation $\Delta G(X)$ in eq 10 denotes the free energy of formation of species X. The three contributions in eq 10 arise because water is only slightly dissociated (0.83 eV), the ion $H_2O^+(aq)$ is unstable (0.5 eV), and the reorganization free energies of OH and H_2O^+ ions are different (0.28 eV).

Anions

The threshold energies of the anions studied thus far^{7,21} are in the 7.2 to 9.2 eV range (Table I). These energies will be correlated to gas-phase electron affinities in the case of univalent anions. Consider the reactions



involving the change of free energy $-\Delta G_s$, $-\Delta G_a$ and ΔG_n , respectively.

The sequence of reactions 11 to 13 is equivalent to the adiabatic process involving the change of free energy $\Delta G_e + \Delta G_r$ (cf. eq 1 and 2). Hence, one has

$$\Delta G_e = -\Delta G_a + \Delta G_n - \Delta G_s - \Delta G_r. \quad (14)$$

Equation 14 will be simplified. The term ΔG_n (< 0.1 eV in absolute value) and the contribution from vibrational relaxation to ΔG_r (a few tenths of electronvolt) can be neglected to a first approximation. The equation $\Delta G_r \approx \Delta G_s/2$ holds for $A^-(aq)$ ions. The electron affinity EA of A(g) is the negative enthalpy of electron attachment, and one has $EA = -\Delta H_a \approx -\Delta G_a$. Equation 14 becomes with these simplifications, $\Delta G_e \approx EA - (3/2)\Delta G_s$ (within ca ± 0.5 eV).

Since one has $EA > 0$ and $\Delta G_s < 0$, ΔG_e is the sum of two positive quantities. Extreme values²² of EA for the anions studied thus far are 1.83 eV for OH and 5.82 eV for ClO_4^- . The ions OH^- and ClO_4^- nevertheless have by coincidence the same threshold energy (8.45 eV) because the difference

of electron affinity is compensated by the difference between the real free energies of solvation. The halides Cl^- , Br^- , I^- represent intermediate cases in which the contributions from EA (3.61, 3.36, 3.06 eV) and $-\Delta G_s$ (3.46, 3.18, 2.81 eV) are similar for each of these three anions.

Threshold energies have also been correlated to the energy E_{\max} at the maximum of the absorption bands of anions exhibiting charge transfer to the solvent.⁷ The correlation between E_t and E_{\max} is approximately linear in agreement with the relationship, $E_t \approx E_{\max} + 1.7$ (in eV), predicted¹¹ from a model for this type of charge transfer spectra.

Cations

Threshold energies of cations M^{z+} (Table I) will be correlated to the gas-phase ionization potentials I^z of the M^{z+} ions just as values of E_t for anions were correlated to gas-phase electron affinities. The following relationship holds⁸

$$\Delta G_e^z = \Delta G_i^z + \Delta G_s^{z+1} - \Delta G_s^z - \Delta G_r^{z+1}, \quad (15)$$

where G_i^z is the free energy for the gas-phase ionization of M^{z+} and the superscript represents the ionic charge. Equation 15 is similar to eq 14. The right hand side of eq 15, except for $-\Delta G_r^{z+1}$, is equal (cf. eq 5) to $\Delta G_H^z + \Delta G^z$, where ΔG^z is the free energy change for the oxidation of M^{z+} to $M^{(z+1)+}$ in a reaction similar to eq 3. The free energy ΔG_i^z can be calculated from ΔG^z , ΔG_s^z , ΔG_s^{z+1} , but the necessary data are generally not available, and one simply equates ΔG_i^z to the ionization potential I^z (enthalpy).

One has for the cations of Table I: $I^z = 20, 30$ to $37, 43$ to 57 eV, respectively, for $z = 1, 2, 3$; $-\Delta G_s^z = 3.5$ to $5, 15.5$ to $21, 42$ to 45 eV, respectively, for $z = 1, 2, 3$; $-\Delta G_r^{z+1} < \text{ca } 2.5$ eV. Equation 15 therefore involves the difference of relatively large numbers in comparison with

ΔG_e^Z . There is partial cancellation of the terms, and the range of E_t^Z values in Table I is only ca 2.5 ev. Data for emission by Fe^{2+} are typical: $\Delta G_e^2 \approx E_t^2 = 7.38$ ev (Table I), $\Delta G_i^2 = 30.51$ ev (calculated from $\Delta G^2 = 0.77$ ev; compare with $I^2 = 30.64$ ev), $\Delta G_s^2 = -19.63$ ev, $\Delta G_s^3 = -44.87$ ev, and $\Delta G_r^3 = -2.11$ ev (from eq 15).

Equation 15 suggests a simple correlation between E_t^Z and I^Z in a series of cations provided the algebraic sum of other terms in this equation is nearly constant. This is the case for the cations of the five metals of Figure 5. The correlation between E_t^2 and I_t^2 is even more striking if the threshold energies are corrected for the difference ΔE_f in the ligand field stabilization energies for the M^{3+} (aq) and M^{2+} (aq) hexaquo ions in an octahedral field⁸ (ΔE_f calculated from data in reference 23).

Weak Acids and Bases and Their Ions

Weak acids in most cases have higher threshold energies than their anions, and conversely weak bases have lower threshold energies than their cations²¹ (Table I). These observations can be accounted for by the method of analysis used for water and hydroxide ion. One has for the acid HA and its anion A^- ,

$$E_t(HA) - E_t(A^-) = [\Delta G(A^-) - \Delta G(HA)] + [\Delta G(HA^+) - \Delta G(A)] \\ + [\Delta G_r(A) - \Delta G_r(HA^+)], \quad (16)$$

where $\Delta G(X)$ represents the free energy of formation of species X. Equation 16 is similar to eq 10 for water and hydroxide ion. Each of the three terms on the right hand side of eq 16 will be examined.

One has $\Delta G(A^-) - \Delta G(HA) = \Delta G_K = -0.0592 \log K$, where ΔG_K is expressed in electronvolts and K is the dissociation constant of HA. Since $K > 10^{-5}$ for the acids of Table I, one has $\Delta G_K < 0.3$ ev. The term $\Delta G_r(A) - \Delta G_r(HA^+)$ should not exceed a few tenths of electronvolt at most because the ions HA^+ and A^- have the same charge in absolute value and

have comparable sizes. Moreover, the contributions from vibrational relaxation should nearly cancel out. The difference of reorganization free energies therefore can be neglected in eq 16 to the approximation of a few tenths of electronvolt. The term $\Delta G(HA^+)$ - $\Delta G(A)$ in eq 16 is the change of free energy for the protonation reaction $H^+ + A = HA^+$ involving the products of the photoionization of A^- and HA . Inspection of the values of E_t in Table I shows (with $\Delta G_K < 0.3$ eV) that this change of free energy is positive. Thus, the ion HA^+ is unstable and the radical A does not protonate to any significant extent in aqueous solution. This analysis is extended in reference 21 to the acids H_nA ($n = 2, 3$) and their anions.

Equation 16 can be transposed to the difference between the threshold energies $E_t(B) - E_t(HB^+)$ of a base B and its cation BH^+ . The difference between the free energies of formation $\Delta G(BH^+) - \Delta G(B) = \Delta G_K$ is negative. One has (in electronvolts) $\Delta G_K = -0.0592 \log K_p$, where K_p is the equilibrium constant for the protonation reaction $B + H^+ = BH^+$. One has, for instance, $\Delta G_K = -0.64$ eV for triethylamine (Table I). The difference between the reorganization free energies $\Delta G_r(BH^{2+}) - \Delta G_r(B^+)$ is negative and not negligible (perhaps -0.5 eV) because of the difference in ionic charge of the species involved (and despite dielectric saturation). Conversely, the quantity $E_t(B) - E_t(HB^+) - \Delta G_K$ for the bases and cations of Table I are quite small, e.g., -0.20 eV for triethylamine. One concludes from these considerations that the quantity $\Delta G(B^+) - \Delta G(BH^+)$ is positive. This quantity is the change of free energy for the dissociation $BH^{2+} = H^+ + B^+$, and consequently BH^{2+} is stable and B^+ protonates provided the pH is not too high. The case of ethylenediamine (Table I) and its cation BH_2^{2+} can be analyzed in a similar way.²¹

Conclusion

The approach in the photoelectron emission spectroscopy of aqueous solutions is simple and direct in its essence: determine threshold energies and interpret (eq 5) the results in terms of free energies for adiabatic oxidation (ΔG) and reorganization (ΔG_r). Conditions for aqueous solutions are particularly favorable because of the high threshold energy (10.06 eV) of water, but application to other solvents and a variety of solutes should be feasible and interesting.²⁴

Our work on photoelectron emission spectroscopy was supported by the Office of Naval Research and the National Science Foundation.

References

- (1) I. Watanabe, J. B. Flanagan and P. Delahay, *J. Chem. Phys.*, 73, 2057 (1980).
- (2) R. M. Noyes, *J. Am. Chem. Soc.*, 84, 513 (1962); 86, 971 (1964).
- (3) B. Case and R. Parsons, *Trans. Faraday Soc.*, 63, 1224 (1967).
- (4) A. Henglein, *Ber. Bunsenges. Physik. Chem.*, 78, 1078 (1974); 79, 129 (1975).
- (5) A. J. Frank, M. Grätzel and A. Henglein, *Ber. Bunsenges. Physik. Chem.*, 80, 593 (1976).
- (6) R. E. Ballard, *Chem. Phys. Lett.*, 42, 97 (1976).
- (7) K. von Burg and P. Delahay, *Chem. Phys. Lett.*, 78, 287 (1981).
- (8) P. Delahay, K. von Burg and A. Dziedzic, *Chem. Phys. Lett.*, 79, 157 (1981).
- (9) P. Delahay and K. von Burg, *Chem. Phys. Lett.*, submitted.
- (10) B. Baron, P. Chartier, P. Delahay and R. Lugo, *J. Chem. Phys.*, 51, 2562 (1969).

- (11) P. Delahay, P. Chartier and L. Nemec, J. Chem. Phys., 53, 3126 (1970).
- (12) P. Delahay, J. Chem. Phys., 55, 4188 (1971).
- (13) L. Nemec, J. Chem. Phys., 59, 6092 (1973).
- (14) H. Aulich, P. Delahay and L. Nemec, J. Chem. Phys., 59, 2354 (1973).
- (15) A. M. Brodsky and A. V. Tsarevsky, J. Chem. Soc. Faraday Trans. II 72, 1781 (1976).
- (16) Yu. Ya. Gurevich, Yu. V. Pleskov and Z. A. Rotenberg,
"Photoelectrochemistry," translation by H. S. Wroblowa, Consultants
Bureau, New York, 1980, pp. 196-198.
- (17) Yu. V. Pleskov, J. Electroanal. Chem., 105, 227 (1979).
- (18) P. R. Bevington, "Data Reduction and Error Analysis for the Physical
Sciences," McGraw-Hill, New York, 1969, p. 199.
- (19) L. Nemec and P. Delahay, J. Chem. Phys., 57, 2135 (1972).
- (20) B. Case in "Reactions of Molecules and Electrodes," N. S. Hush, Ed.,
Wiley-Interscience, New York, 1971, pp. 45-134.
- (21) K. von Burg and P. Delahay, Chem. Phys. Lett., submitted.
- (22) L. G. Christophorou, "Atomic and Molecular Radiation Physics," Wiley-
Interscience, New York, 1971, pp. 546-551, 565-571.
- (23) T. M. Dunn, D. S. McClure and R. C. Pearson, "Crystal Field Theory,"
Harper and Row, New York, 1965, p. 82.
- (24) Nonaqueous solvents of low vapor pressure were in fact used in earlier
work²⁵ (not reviewed here) on energy distribution curves. Such
solvents were not used thus far in the determination of threshold
energies although some of the earlier emission spectra could be analyzed
for that purpose.
- (25) L. Nemec, L. Chia and P. Delahay, J. Phys. Chem., 79, 2935 (1975).

Table I

Threshold Energies of Aqueous Solutions^{a,b} OH^- (8.45), H_2O (10.06) Cl^- (8.81), Br^- (8.05), I^- (7.19) ClO_3^- (8.21), BrO_3^- (7.88), IO_3^- (7.44), ClO_4^- (8.45) SO_3^{2-} (7.17), $\text{S}_2\text{O}_3^{2-}$ (7.27), SO_4^{2-} (8.65), $\text{S}_2\text{O}_8^{2-}$ (7.33) NO_2^- (7.57), NO_3^- (7.46), N_3^- (7.35) H_3PO_4 (9.45), $\text{H}_2\text{PO}_4^{2-}$ (9.23), HPO_4^{2-} (8.79), PO_4^{3-} (7.44) H_3AsO_4 (9.44), H_2AsO_4^- (9.09), HAsO_4^{2-} (8.50), AsO_4^{3-} (8.30) HOO_3^- (9.07), CO_3^{2-} (7.40), CNS^- (7.20) Sn^{2+} (7.42), Pb^{2+} (7.23), In^{3+} (7.15), Tl^+ (7.40) Cu^{2+} (7.83), Ag^+ (7.60) Ni^{2+} (8.35), Co^{2+} (8.60) Fe^{2+} (7.38), Fe^{3+} (7.03) Mn^{2+} (8.08), Cr^{2+} (6.14), Cr^{3+} (7.33) V^{2+} (6.38), V^{3+} (7.06), Ti^{3+} (6.90)

Weak acids and anions: formic (10.0, 7.55), acetic (9.00, 7.82), propionic (9.08, 8.42), n-butyric (8.99, 8.23), oxalic (8.26, 7.50, 7.32), tartaric (8.55, 7.72, 7.37), citric (8.66, 8.52, 8.39, 7.48)

Weak bases and cations: triethylamine (6.73, 7.57), aniline (7.39, 8.44) ethylenediamine (7.20, 7.47, 8.13)

^a Values of E_t in electronvolts. Standard deviation of 0.01 to 0.03 eV in general.^{7-9,21} ^b Results for cations generally obtained with chloride or perchlorate solutions.

Captions to Figures

Figure 1. Schematic diagram of instrument for the determination of emission spectra.¹

Figure 2. Photoelectron emission spectrum of liquid water at 1.5°C (curve A) and plot of $y^{0.5}$ against E (line B). Statistical F-test of exponent of the yield in inset.⁹ $F = R^2(N - 2)/(1 - R^2)$, where R is the correlation coefficient for least square fitting and N the number of points.

Figure 3. Plot of threshold energy and reorganization free energy against the free energy⁸ $\Delta G = |e|E^\circ$ (E° standard reduction potential for the M^{3+}/M^{2+} couple).

Figure 4. Free energies of formation and free energy changes (in electronvolts) for photoelectron emission by water and hydroxide ion.⁹

Figure 5. Correlation between ionization potential and threshold energy corrected for the difference ΔE_f between the ligand field stabilization energies for M^{3+} and M^{2+} in an octahedral field.⁸

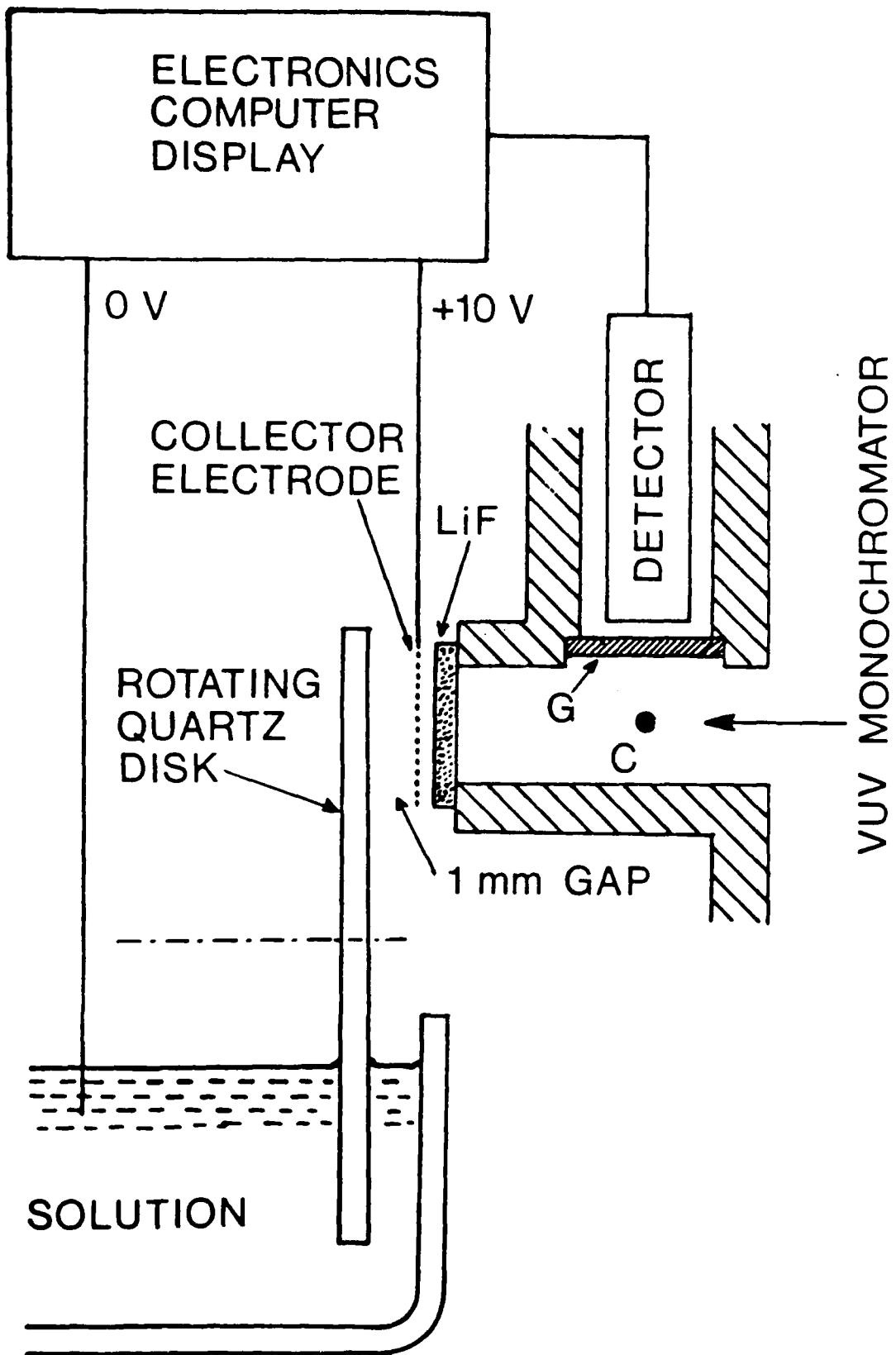


FIG. 1

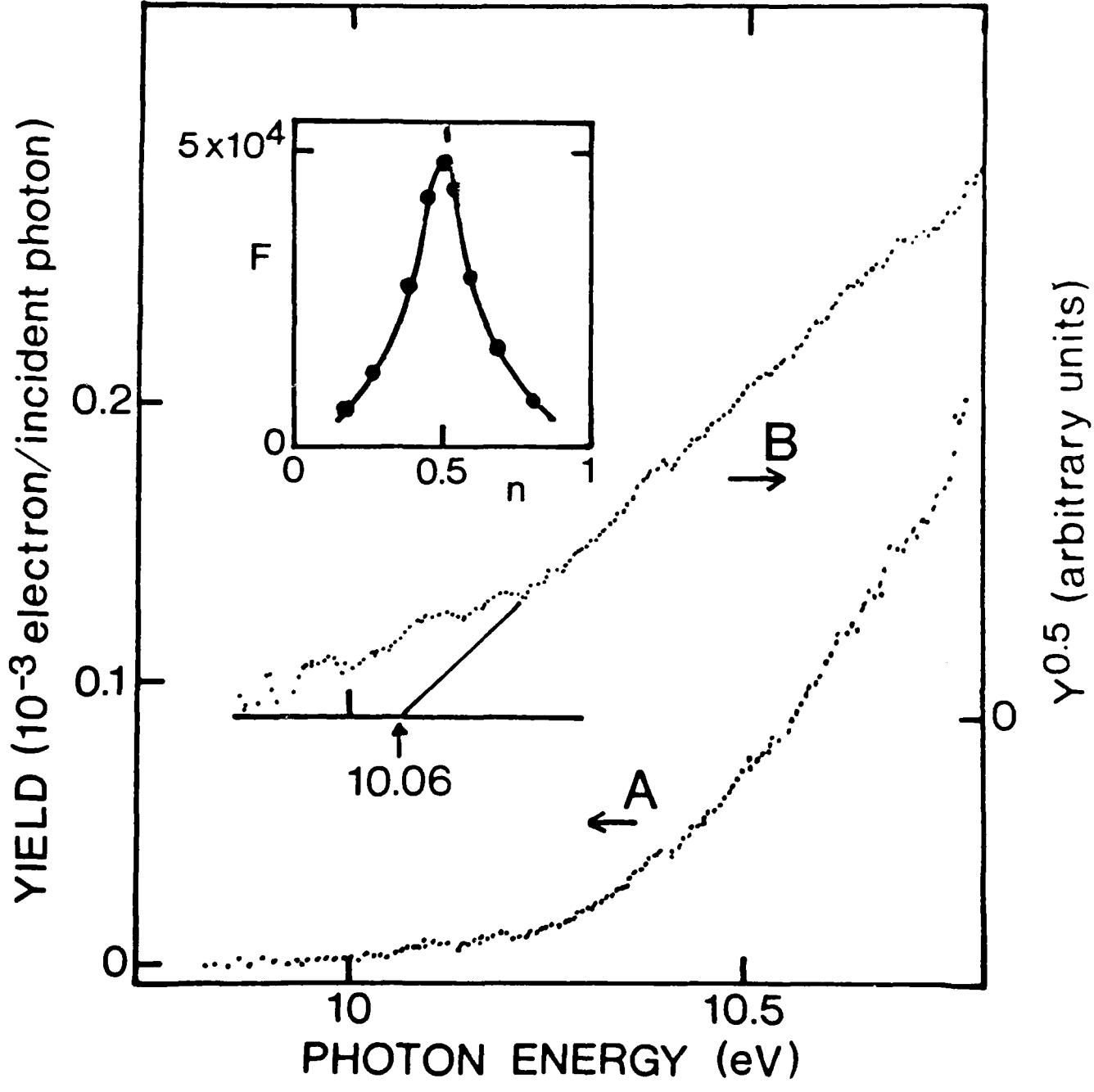


FIG. 2

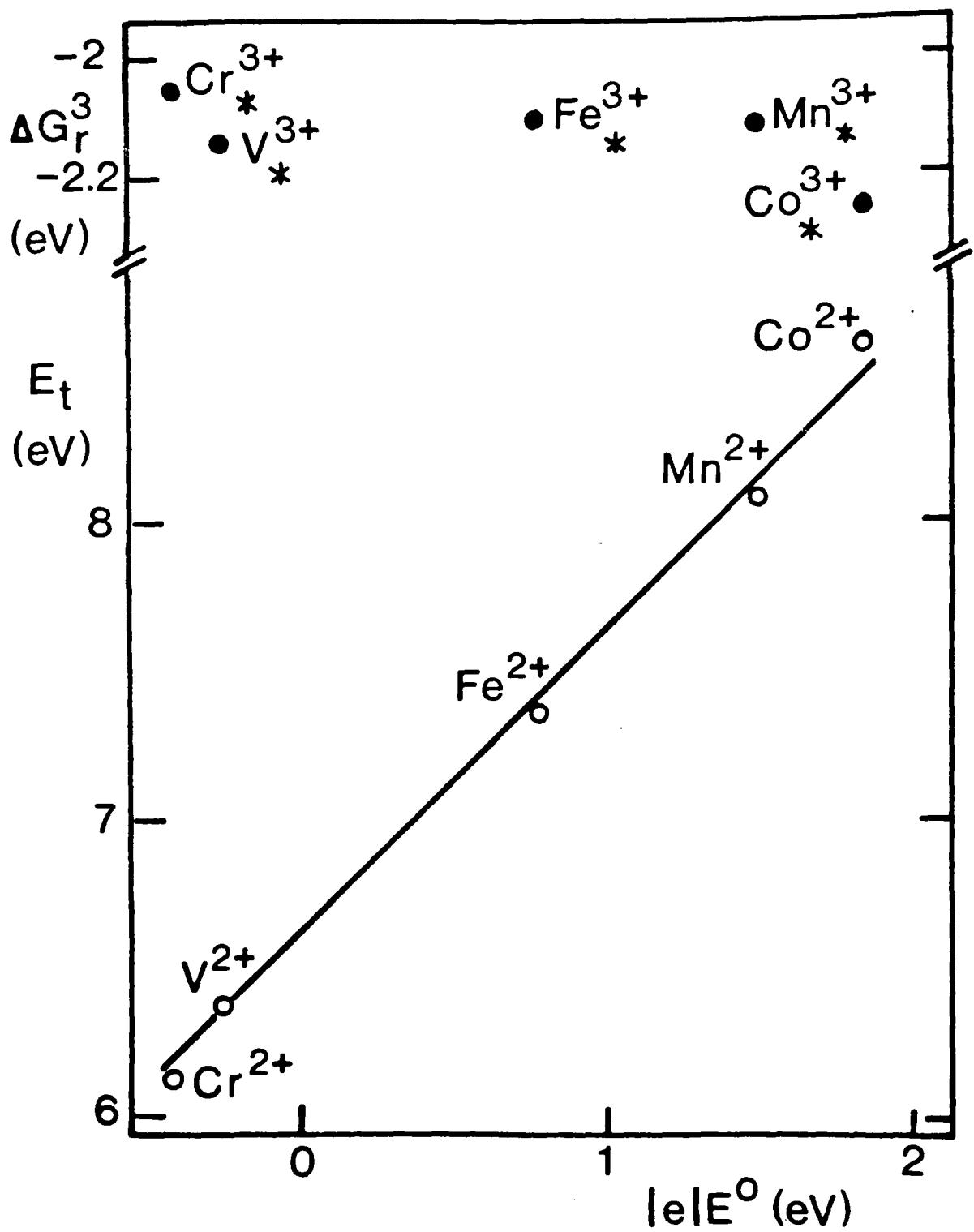


FIG. 3

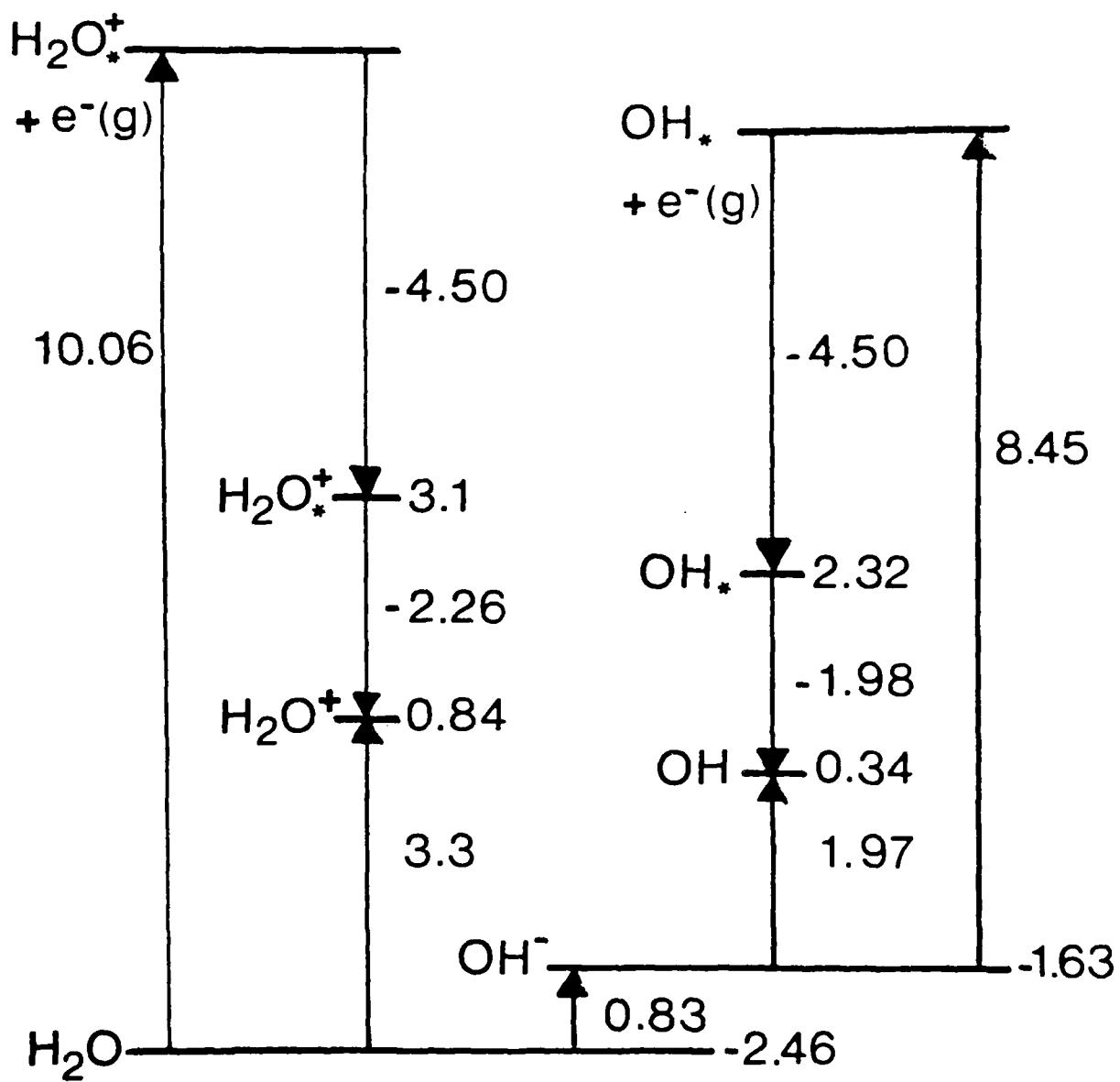


FIG. 4

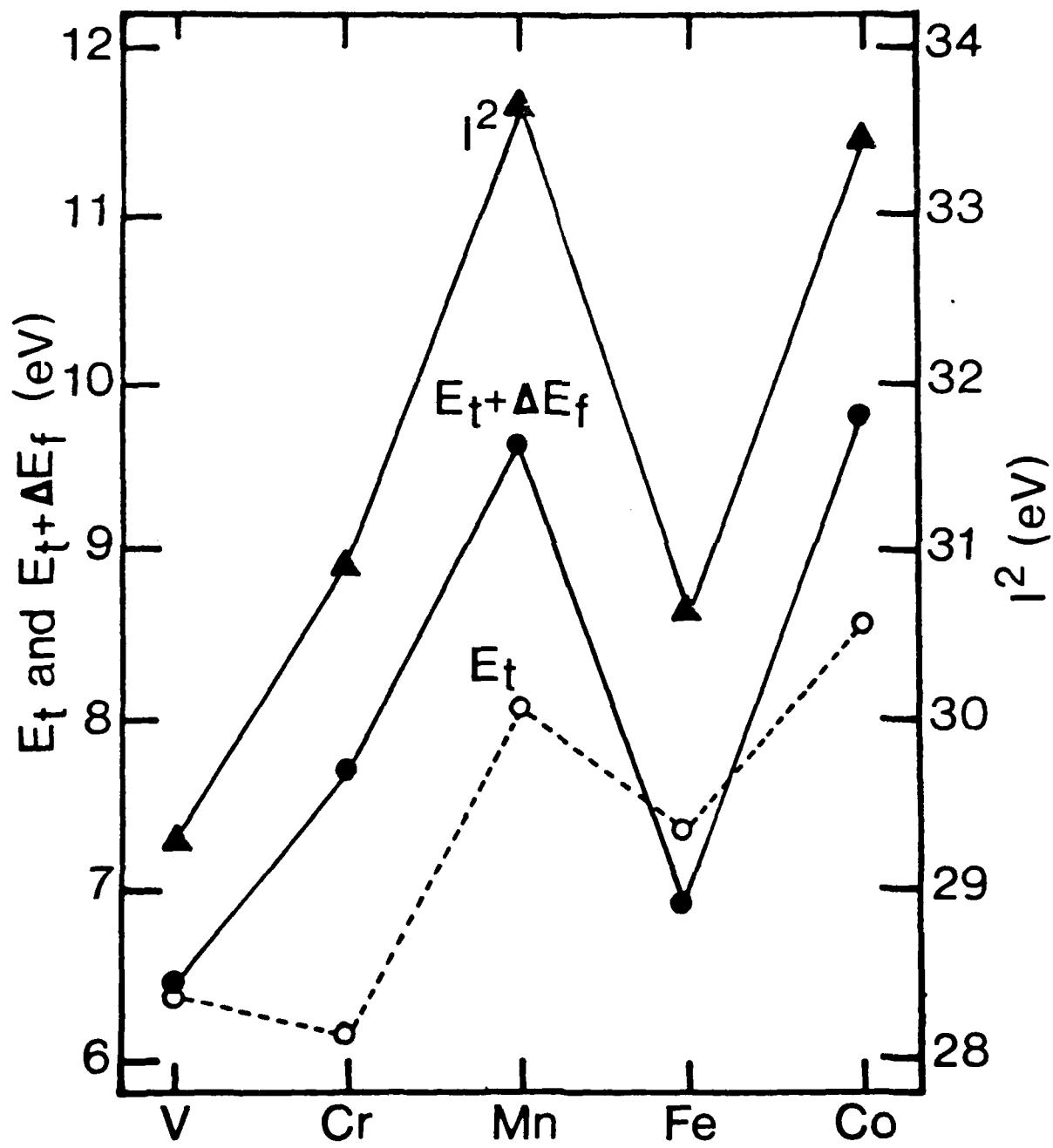


FIG. 5

TECHNICAL REPORT DISTRIBUTION LIST, GEN

<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>	
	Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709 1
	ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152 1
	ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555 1
	ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401 1
	ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940 1
	Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380 1
	The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217 1
	Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401 1
	Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232 1
	Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112 1

TECHNICAL REPORT DISTRIBUTION LIST, GEN

No.
Copies

Dr. Rudolph J. Marcus Office of Naval Research Scientific Liaison Group American Embassy APO San Francisco 96503	1
Mr. James Kelley DTNSRDC Code 2803 Annapolis, Maryland 21402	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 41106	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152
Dr. J. J. Auborn Bell Laboratories Murray Hill, New Jersey 07974	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201
Dr. T. Katan Lockheed Missiles & Space Co., Inc. P.O. Box 504 Sunnyvale, California 94088	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>	
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton SO9 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>		
	Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
	Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonices Division Naval Weapons Support Center Crane, Indiana 47522	1
	Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
	Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
	Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
	Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1		
	Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		

TECHNICAL REPORT DISTRIBUTION LIST, 051B

<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>		
Professor K. Wilson Department of Chemistry, B-014 University of California, San Diego La Jolla, California 92093	1	Dr. B. Vonnegut State University of New York Earth Sciences Building 1400 Washington Avenue Albany, New York 12203	1
Professor C. A. Angell Department of Chemistry Purdue University West Lafayette, Indiana 47907	1	Dr. Hank Loos Laguna Research Laboratory 21421 Stans Lane Laguna Beach, California 92651	1
Professor P. Meijer Department of Physics Catholic University of America Washington, D.C. 20064	1	Dr. John Latham University of Manchester Institute of Science & Technology P.O. Box 88 Manchester, England M601QN	1
Dr. S. Greer Chemistry Department University of Maryland College Park, Maryland 20742	1		
Professor P. Delahay New York University 100 Washington Square East New York, New York 10003	1		
Dr. T. Ashworth Department of Physics South Dakota School of Mines & Technology Rapid City, South Dakota 57701	1		
Dr. G. Gross New Mexico Institute of Mining & Technology Socorro, New Mexico 87801	1		
Dr. J. Kassner Space Science Research Center University of Missouri - Rolla Rolla, Missouri 65401	1		
Dr. J. Telford University of Nevada System Desert Research Institute Lab of Atmospheric Physics Reno, Nevada 89507	1		

N
DATE